

# Enhanced microbial activity in carbon-rich pillow lavas, Ordovician, Great Britain and Ireland

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## ABSTRACT

There is extensive evidence for the microbial colonization of seafloor basalts in the modern ocean and in the geological record. The sulfur isotope composition of pyrite in the basalts commonly indicates marked isotopic fractionation due to microbial sulfate reduction. Sections through the *Nemagraptus gracilis* zone (Ordovician) in Great Britain and Ireland are characterized by both widespread pillow lavas and organic-rich seafloor sediment, allowing an exceptional opportunity to assess whether the availability of organic carbon influenced the extent of microbial activity in the basalts in deep geological time. Whole-rock data from basalts at 10 localities show that there is a relationship between sulfur isotopic composition and the carbon content of the basalt. At two localities where organic carbon was entrained in the basalt, isotopic compositions are heavy compared to compositions in carbon-poor basalt, implying that microbial activity exhausted the supply of seawater sulfate. In most basalt, microbial activity was limited by the supply of carbon, but where the basalt incorporated carbon during emplacement on the seafloor, microbial activity became sulfate limited.

## INTRODUCTION

The igneous crust at and below the seafloor may represent one of the largest residences for life on Earth. It is the largest aquifer (Edwards et al., 2011, 2012), and may support an extensive microbial community (Heberling et al., 2010), which before the evolution of land plants would have overwhelmingly dominated the planet's biomass. Microbial activity is facilitated by extensive fluid flow, and water-rock interaction, to provide nutrient and energy sources (Edwards et al., 2011). Evidence for microbial life in this setting today comes from the microbiology and molecular biology of isolates from cores through the ocean floor (Fry et al., 2008; Edwards et al., 2012; Lever et al., 2013). There is also evidence from minerals precipitated by microbial activity, including the iron sulfide pyrite found in vesicular basalts below the seafloor of most of the world's oceans (Parnell et al., 2014a). Pyrite is present in the deep geological record, and so can provide us with a record of microbial colonization of the subseafloor igneous crust, based on the sulfur isotopic composition of the pyrite, which reflects isotopic fractionation associated with microbial sulfate reduction. Thus, the isotopic composition of pyrite in modern and ancient basalts has been used to prove subseafloor microbial activity (e.g., Rouxel et al., 2008; McLoughlin et al., 2012; Lever et al., 2013; Parnell et al., 2014a).

An important constraint for subseafloor life, especially in igneous crust, is the availability of organic carbon to provide biomass in heterotrophic organisms. Genetic studies show that active carbon cycling occurs (Edwards et al., 2011). Buried organic matter, in sediments deposited on the seafloor, can provide the necessary carbon

(Wellsbury et al., 1997; Edwards et al., 2012), but it is not always accessible to the igneous crust. However, in the geological record, there are episodes when seafloor volcanism occurred within periods of organic-rich sedimentation to leave basalts accompanying black shales. This occurred particularly during the Ordovician, which was a period of both anomalous seafloor volcanic activity and black shale sedimentation (Vaughan and Scarrow, 2003), exemplified in

the *Nemagraptus gracilis* zone (Sandbian Stage, Ordovician) rocks of Britain and Ireland. In Scotland, Republic of Ireland, Northern Ireland, and Wales, this zone is characterized by black shales (Leggett, 1978) and also includes pillow lavas at numerous localities (Fig. 1; sample details are provided in the GSA Data Repository<sup>1</sup>). The pillow lavas are typically basalts consisting of a largely feldspathic groundmass with traces of interstitial opaque minerals (mostly magnetite, some pyrite). At two localities there is evidence that, during emplacement of the pillow lavas, the magma interacted with organic-rich sediment to produce mobile hydrocarbons, which on cooling left a solid carbonaceous residue within basalt. At Helen's Bay, Northern Ireland (locality in Craig, 1984), the basalt contains numerous clusters of carbon blebs and stringers, associated with chlorite and titanium oxide (Fig. 2), and millimeter-scale fragments of

<sup>1</sup>GSA Data Repository item 2015279, sample locations and isotope data, is available online at [www.geosociety.org/pubs/ft2015.htm](http://www.geosociety.org/pubs/ft2015.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.



**Figure 1. Localities for pillow lavas analyzed in this study. All localities are specifically in the Ordovician *Nemagraptus gracilis* zone, except Gorumna, Rhiw, and Bennane, which are less specifically dated to the Middle Ordovician.**

black shale. At Llanwrtyd Wells, Wales (locality in Stamp and Wooldridge, 1923), the basalt contains millimeter-scale quartz with domains of chlorite intermixed with carbon (Fig. 2), in which the uniform distribution of the carbon in the chlorite indicates that it had unmixed from a carbon-silicate fluid. In both cases, the basalt is crosscut by veinlets of solid carbon (bitumen). The incorporated carbon has resulted in organic carbon contents of as much as 0.21% in the basalts. Basalts from five other localities in the *N. gracilis* zone, and three localities less specifi-

cally dated to the Middle Ordovician (Fig. 1), where no interaction with organic-rich sediment occurred, have organic carbon contents of 0.03%–0.08%. Sulfur in the basalts occurs as pyrite, in vesicle fills, and crystals disseminated through the groundmass. The occurrence of both carbon-rich and carbon-poor basalts of the same age provides an exceptional opportunity to investigate if the carbon influenced the degree of microbial activity in the lavas, as measured by their sulfur isotope composition.

## METHODS AND DATA

Whole-rock samples of basalts from the 10 localities were measured for sulfur isotope composition, using the chromium reduction method of Canfield et al. (1986). The  $H_2S$  generated from the reduction of sulfide sulfur by  $CrCl_2$  was trapped as  $Ag_2S$  in  $AgNO_3$  solution. The resulting sulfide was washed, dried, and analyzed by conventional procedures, following the method of Robinson and Kusakabe (1975). For carbonate stable isotope analysis, 1 mg sample powders were dissolved overnight in phosphoric acid at 70 °C. Ratios were measured on an AP2003 mass spectrometer. Repeat analyses of the NBS-18 standard are generally better than  $\pm 0.2\text{‰}$  for carbon and  $0.3\text{‰}$  for oxygen. Organic carbon contents were measured using a LECO CS225 elemental analyzer, after decarbonatization with hydrochloric acid, to a precision of  $\pm 0.05\%$ . The structural order of the carbon in the basalts and associated shale successions was characterized by laser Raman spectroscopy, using a Renishaw inVia reflex Raman spectrometer, with an Ar+ green laser (wavelength 514.5 nm). Initial analyses were based on accumulations over 3 s scan time on 10% laser power. The extended spectra were based on four spectra each, accumulated over 10 s scan time with 10% laser power.

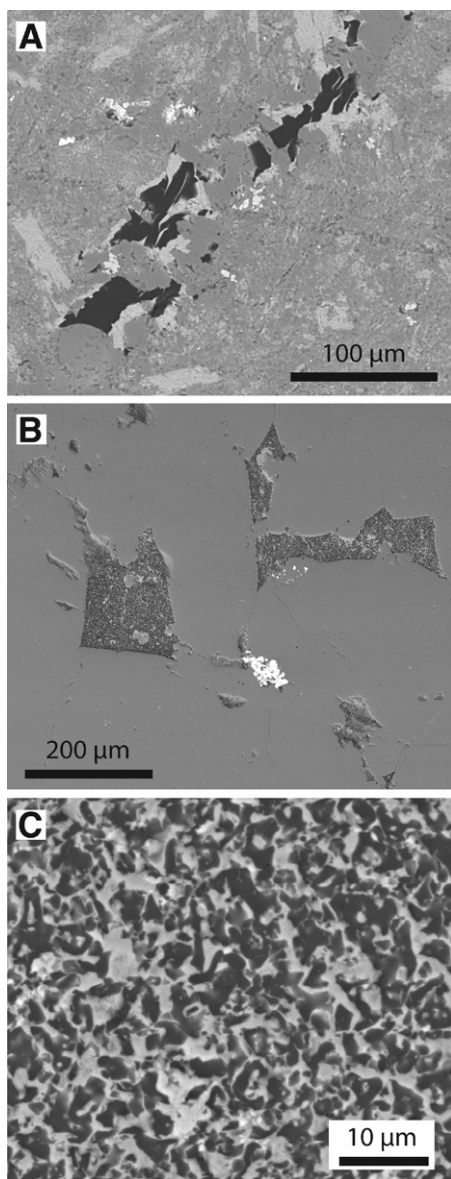
The 8 low-carbon basalts ( $<0.1\%$  total organic carbon, TOC) yielded  $\delta^{34}S$  values from  $-25\text{‰}$  to  $+5\text{‰}$ , to a precision of  $\pm 1\text{‰}$  (see the Data Repository). The 2 carbon-bearing basalts

( $>0.1\%$  TOC) yielded heavier compositions from  $+14\text{‰}$  to  $+42\text{‰}$  (Fig. 3). The data set as a whole shows a correlation of heavier (more positive) sulfur isotope composition with higher carbon contents of  $>0.1\%$  TOC (Fig. 3). Analyses of discrete pyrite crystals in the Llanwrtyd Wells basalt yield comparable compositions of  $+22\text{‰}$  to  $+23\text{‰}$ . Analyses of 6 samples of calcite from vesicles in low-carbon basalts yielded a mean carbon composition of  $0.0\text{‰}$  and oxygen composition of  $-7.2\text{‰}$ , and 7 samples of calcite from carbon-bearing basalt yielded a mean carbon composition of  $-10.8\text{‰}$  and oxygen composition of  $-12.2\text{‰}$  (see the Data Repository). The two sets of data are quite distinct (Fig. 4). Raman spectra for the carbon in both the basalt and shales exhibit well-developed order (G) and disorder (D) peaks, indicating that the carbon is disordered (Fig. DR1 in the Data Repository), and has a composition referable to kerogen as defined by Wopenka and Pasteris (1993), rather than graphite. This is consistent with conodont alteration indices of  $\sim 5$  for both localities, characteristic of low-grade metamorphism (Bergström, 1980). Raman spectra for fluid inclusions in crosscutting mineral veins at Helen's Bay, and Middle Ordovician seafloor volcanic rocks at Builth Wells, near Llanwrtyd Wells, show volatile hydrocarbons to  $C_5$  (Metcalfe et al., 1992; Parnell et al., 2014b).

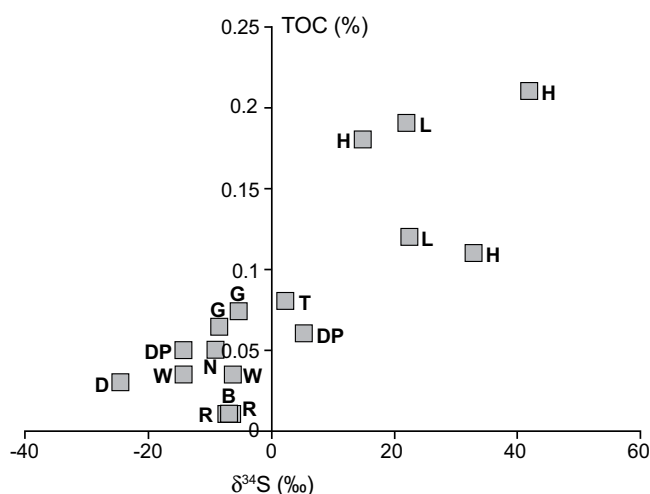
## DISCUSSION

### Sulfur and Carbon Isotope Fractionation

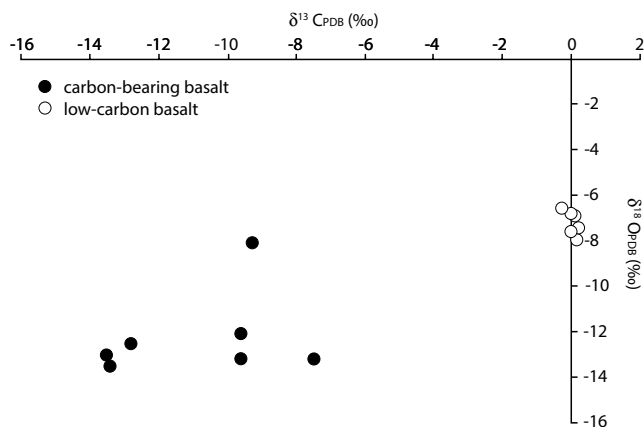
The sulfur isotope compositions of the basalts can be interpreted in terms of microbial activity in the basalts. The low-carbon samples yielded a range of isotopic values to as low as  $-25\text{‰}$ , representing a variable mixture of isotopically light sulfur compositions reflecting microbial reduction of seawater sulfate and near-zero isotopic compositions reflecting a magmatic origin. The light compositions are fractionated from Ordovician seawater sulfate



**Figure 2.** Backscattered electron micrographs of carbon in Ordovician basalts. A: Basalt containing stringers of carbon (dark) and adjacent chlorite (gray), Helen's Bay, Northern Ireland. B: Quartz (gray) containing carbon-chlorite masses (dark) and pyrite (bright), Llanwrtyd Wells, Wales. C: Detail of carbon-chlorite masses in B, showing homogeneous intermixture of carbon (dark) and chlorite (light).



**Figure 3.** Cross-plot of whole-rock sulfur isotope composition and organic carbon content for Ordovician basalt samples. Data show general trend of heavier isotopic composition with higher carbon content. B—Bennane; D—Duncannon; DP—Downan Point; G—Gorumna; H—Helen's Bay, L—Llanwrtyd Wells; N—Noblehouse; R—Raven Gill; T—Tra-more; W—Rhiw.



**Figure 4. Cross-plot of carbon and oxygen stable isotope compositions for calcite samples from carbon-bearing basalts (solid circles,  $n = 7$ ) and low-carbon basalts (open circles,  $n = 6$ ). Calcite from carbon-bearing basalt is isotopically light, consistent with microbial processing of organic matter. For sample details, see the Data Repository [see footnote 1]. PDB—Pee Dee belemnite.**

(+25‰ to +30‰; Claypool et al., 1980) to a degree far greater than is possible by abiotic processes (Machel, 2001). A larger data set, for pyrite crystals separated from Ordovician basalts, yielded a similar range of values (Parnell et al., 2014a). The carbon-bearing basalts have isotopic compositions heavier than could be explained by a magmatic origin for the sulfur, which would be characterized by near-zero values. Rather, the relatively heavy composition is typical of settings where the sulfate is progressively fractionated in a closed system to yield isotopically light sulfide (which may escape as hydrogen sulfide) and heavy residual sulfate, which then influences the composition of later formed sulfides (Schwarcz and Burnie, 1973; Fallick et al., 2012). This represents a greater degree of fractionation of the sulfate than in the low-carbon samples, and implies the immediate availability of organic carbon to further microbial activity. There is evidence from other subsurface environments to show that sulfate reducers can utilize geological carbon in anaerobic conditions, including oil reservoirs (Rueter et al., 1994), coal deposits (Wawrik et al., 2012), and black shales (Machel, 2001). These occurrences offer strong support for the inference that basalt containing organic carbon would support sulfate-reducing microbial activity.

Secondary calcite mineralization in the basalts occurs as vesicle and fracture fillings. The isotopic composition of carbon in the calcite can indicate whether the carbon was derived from organic carbon or seawater bicarbonate. Samples of calcite from the carbon-bearing basalts at Llanwrtyd Wells and Helen's Bay have carbon isotope compositions quite distinct from samples of calcite from the carbon-poor basalts at Duncannon, Duncannon Point, and Noblehouse (Fig. 4). The calcite from the carbon-bearing basalt is isotopically light, suggesting that this could be the result of biological processing, while the calcite in the other samples is near zero, similar to seawater composition. These data are strongly consistent with utilization of the carbon in the carbon-bearing basalts by microbial activity.

### Magma-Sediment Interaction

The samples represent variable degrees of interaction between magma and sediment. It has become clear that much lava is actually emplaced within wet sediment, causing intermingling of the two components (Hole et al., 2013) in a quasi-intrusive relationship. Where the sediment is organic rich, this resulted in the generation of hydrocarbons. The potential for interaction with organic-rich sediment was particularly high during the Ordovician because of the relative abundance of both basalts and black shales in the same section, but other examples of hydrocarbons in seafloor basalts in the geological record show that these interactions are not exceptional. There are numerous examples of carbon segregation through interaction between intrusive igneous rocks and organic-rich sediments, as found in the North Atlantic region where Mesozoic shales are altered by Paleocene intrusions (e.g., Lindgren and Parnell, 2006), and in intrusion-related hydrothermal systems on the current seafloor (Kvenvolden and Simoneit, 1990). Mixing within the sediment, rather than at the surface, explains how the high temperature was maintained to allow carbon to become incorporated in the melt at Llanwrtyd Wells.

### Availability of Carbon

Although the carbon in the basalts from Helen's Bay and Llanwrtyd Wells has been at very high temperatures, and in the latter case has been incorporated in a melt, Raman spectroscopy shows that it remained disordered reduced carbon, and thus was potentially reactive. This is consistent with other studies showing that melting and resolidification does not cause carbon to become ordered and thus unreactive (Kadik et al., 2004; Parnell and Lindgren, 2006). The succession also underwent low-grade regional metamorphism during the Caledonian orogeny (Silurian–Devonian), which explains why the carbon in all the basalt and shale samples now has comparable thermal maturity. This implies that the carbon may have been more disordered, and reactive,

before the orogeny. In younger sequences that have not undergone orogenic heating, seafloor volcanic rocks contain liquid oil (Kvenvolden and Simoneit, 1990). At any stage of thermal maturity, the carbon would also release methane. On and below the present-day ocean floor, the methane and higher hydrocarbons in volcanic rocks may support microbial communities (Bazylinski et al., 1989; Lizarralde et al., 2011), and we infer that similar microbial activity was possible below the Ordovician seafloor. More generally, other studies show that a deep biosphere can be supported by organic compounds released from kerogen in lithified rocks (Krumholz et al., 2002). Some of the carbon may have been relatively inert, but the presence of liquid hydrocarbons is suggested by the veinlets of solid carbon, and methane and other volatile hydrocarbons are identified in fluid inclusions, both of which could support microbial activity. The carbon-bearing microfractures through the basalt would have facilitated ready access to microbial life. The low-carbon basalts occur in sequences containing black shales, but do not have immediacy of access to the carbon because the carbon was not intermixed in the basalt.

The evidence from sulfur isotope data combines with evidence from bioalteration (McLoughlin et al., 2012) to show that there is a long-term geological record of microbial activity in subseafloor basalts. Carbonaceous linings to microborings and microbial carbonate precipitates (Furnes et al., 2001) demonstrate the processing of carbon by this activity. Our study emphasizes the importance of carbon availability, and that high carbon contents in basalts can allow a level of microbial activity greater than normal.

### Ordovician Subseafloor Biosphere

This study shows that the incorporation of carbon in Ordovician seafloor basalts allowed them to support anomalous levels of microbial activity. The availability of organic carbon in the subseafloor was high in the early Paleozoic, when the oceans were anoxic (Saltzman, 2005). This enhanced the chance of carbon becoming entrained in basalts and supporting microbial activity within them. Other studies of Ordovician seafloor deposits have shown evidence for microbial activity in carbonated serpentinites (Lavoie and Chi, 2010) and injected sand complexes (Parnell et al., 2013). Future research should investigate whether subseafloor microbial activity has fluctuated through geologic time in conjunction with variations in oceanic oxygenation.

### CONCLUSION

These data emphasize that the cycling of carbon and sulfur in subseafloor basalts may be linked. Previous studies showed the coexistence of methanogens and sulfate reducers in subseafloor basalts (Lin et al., 2012; Lever et al., 2013).

In marine sediments, especially anoxic sediments, the carbon and sulfur cycles are clearly linked, and higher contents of metabolizable organic matter engender higher sulfur contents by supporting more microbial sulfide precipitation (Raiswell and Berner, 1986; Lin and Morse, 1991). Similarly, this study shows that basalts containing organic carbon allowed more sulfur cycling than in normal low-carbon basalts.

## ACKNOWLEDGMENTS

A. Sandison and C. Taylor provided skilled technical support. Boyce is funded by Natural Environment Research Council (NERC) support of the Isotope Community Support Facility at the Scottish Universities Environmental Research Centre. NERC supported the project through facility grant IP-1235-0511. The Raman spectroscopy facility at the University of Aberdeen is funded by the Biotechnology and Biological Sciences Research Council. We are grateful to M. Feely, G. Purvis, and an anonymous reviewer for helpful criticism.

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Manuscript received 2 May 2015

Revised manuscript received 6 July 2015

Manuscript accepted 8 July 2015

Printed in USA